

CATALYZED STEAM GASIFICATION OF LOW-RANK COALS TO PRODUCE HYDROGEN

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Abstract

Advance coal gasification technologies using low-rank coal is a promising alternative for meeting future demand for hydrogen. Steam gasification tests conducted at temperatures between 700° and 800°C and atmospheric pressure resulted in product gas compositions matching those predicted by thermodynamic equilibrium calculations, 63-65 mol% hydrogen and less than 1 mol% methane. Steam gasification tests with four low-rank coals and a single bituminous coal were performed in a laboratory-scale thermogravimetric analyzer (TGA) at temperatures of 700°, 750°, and 800°C to evaluate process kinetics with and without catalyst addition. Catalysts screened included K_2CO_3 , Na_2CO_3 , trona, nahcolite, sunflower hull ash, and recycled lignite ash. North Dakota and Texas lignite chars were slightly more reactive than a Wyoming subbituminous coal char and eight to ten times more reactive than an Illinois bituminous coal char. Pure and mineral (trona and nahcolite) alkali carbonates and recycled ash from K_2CO_3 -catalyzed steam gasification tests substantially improved low-rank coal steam gasification rates. The reactivities obtained using trona and nahcolite to catalyze the steam gasification were the highest, at nearly 3.5 times those without catalysts.

Introduction

Hydrogen is a key component in petroleum refining, petrochemical processing, the production of coal-derived synfuels, and can also be used directly as a fuel. Over the next 45 years, the demand for hydrogen has been projected to increase by a factor of 15 to 20 (1). Most of the hydrogen currently used in chemical applications is produced through steam reforming of natural gas; and in refining applications partial oxidation of petroleum is also used. Advanced coal gasification technologies appear to be the most probable alternative for meeting the future demand for large quantities of hydrogen. Low-rank coals (lignites and subbituminous coals) are candidate feedstocks for such applications because of their low mining cost and higher reactivity relative to higher rank coals.

The two most important considerations in the design of a process for producing hydrogen from coal are to maintain operating conditions that thermodynamically favor the production of hydrogen and carbon dioxide over carbon monoxide and methane, and to obtain reaction rates that result in reasonable gasifier throughput. Optimization of the hydrogen content of the product gas requires steam gasification at relatively mild temperatures in the range of 700° to 800°C and at atmospheric pressure. In tests at the University of North Dakota Energy Research Center (UNDERC), a dry synthesis gas containing 63 mol% hydrogen was produced by steam gasification of low-rank coal (2), which is predicted by equilibrium thermodynamics. These mild conditions do not, however, promote high reaction rates. As a result, achieving the maximum coal reactivity by the use of catalysts is perhaps the most critical factor in producing hydrogen from coal.

The physical and chemical nature of low-rank coals (LRCs) offer several advantages for a gasification process producing hydrogen. One of these is their enhanced reactivity compared to coals of higher rank. This increase in reactivity is caused by higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts (3,4,5).

The high volatile matter content of lignites could also support their use in steam gasification to produce hydrogen. If introduced into the hot zone of a gasifier, devolatilization products may be cracked to form additional hydrogen (6). Under suitable reaction conditions raw product gas from such a system would then contain essentially only hydrogen, carbon dioxide, carbon monoxide, and only small quantities of methane and sulfur gases. In addition to producing hydrogen and simplifying downstream gas clean-up, cracking of tars and oils in the gasifier would also reduce contaminant concentrations in the process condensate.

Even with the higher reactivities of LRCs, it will be necessary to enhance reaction kinetics through the use of catalysts to obtain economic reactor throughput. There is a wealth of data relating to the use of a variety of catalysts to enhance the steam gasification kinetics (7 - 16). Alkali metals are generally accepted as the premier steam gasification catalyst (12,13,16) and thus their interactions with ash constituents and subsequent recovery are important factors in the process economics. Catalyst recovery problems associated with the formation of insoluble potassium aluminosilicates were identified during recovery of the K_2CO_3 catalyst in the Exxon Catalytic Coal Gasification (CCG) process (6). For some high sodium LRCs, a problem of sodium dilution of the recovered potassium catalyst could be significant. However, if sodium carbonates are also effective catalysts, the problem of alkali recovery will be mitigated, especially with high sodium LRCs.

The overall objective of the program at UNDERC is to establish the feasibility of using low-rank coal gasification to produce hydrogen. This paper summarizes the findings of a thermogravimetric analysis (TGA) study of steam-char gasification kinetics. This work focused on low-rank coals, with limited testing using a bituminous coal for comparison purposes, and the addition of various catalysts to enhance low-rank coal reactivity.

Experimental

The reaction between low-rank coal chars and steam was studied using a DuPont 951 Thermogravimetric Analyzer (TGA) interfaced with a DuPont 1090 Thermal Analyzer. The TGA reaction chamber was an open quartz tube, secured to the balance by means of a threaded nut as shown at point (A) in Figure 1. The opposite end of the quartz tube (point (B) in Figure 1) was connected by rubber tubing to a ventilation hood. The commercially available TGA system was modified for char/steam experiments by adding the steam sidearm shown as point (C) in Figure 1. This port was sealed with a high-temperature gas chromatography septum. The steam inlet line (1/8-inch stainless steel) was passed through this septum and into the reaction chamber (point (D) in Figure 1). Steam was prepared using a "Hot Shot" MB-3L electric steam boiler. The length of steam line from the exit of the boiler to the reaction chamber sidearm was heated continuously at 200°C using electrical heat tape. The reaction chamber was heated in a program-controlled tube furnace.

Approximately 20 mg, weighed to the nearest 0.01 mg, of as-received coal ground to particle sizes of -100 x +140 mesh, was evenly distributed on a tared 11-mm diameter platinum pan supported at the end of the TGA's quartz balance beam. Coal samples were devolatilized in argon prior to the introduction of steam into the reaction chamber. Argon flow was maintained at approximately 160 cc/min while the coal sample was heated from room temperature to the target reaction temperature (700° to 800°C) at a rate of 100°C/min. The average time for devolatilization of these samples was about 15 minutes.

Char samples produced by the devolatilization procedure were weighed in the TGA reaction chamber without cooling. Argon flow was reduced from 160 to 60 cc/min, and steam to the reactor was then started at rates of 1-5 mg/min. Steam flow rates were determined prior to experiments by collecting steam from the gas outlet (point (B) in Figure 1) in a cold, tared vessel for approximately 15 minutes.

Weight, time, and temperature were recorded by the DuPont 1090 Thermal Analyzer as the char-steam reaction proceeded. Experiments were terminated when the sample's weight loss approached zero, or in the case of very slowly reacting materials after 150 minutes of reaction time. The 1090 Thermal Analyzer was then used to plot sample weight loss versus time and to print sample weight, temperature, and reaction time data. Product gases from the system were not analyzed.

Both aqueous impregnation and dry catalyst mixing were evaluated in the TGA steam gasification test. Preliminary TGA tests showed that reactivity was not dependent on catalyst addition technique; therefore, only dry-mix systems were used in the remainder of the TGA test program.

Results

The matrix of char-steam gasification tests conducted by laboratory TGA included experiments for evaluation of coals, catalysts, temperature, and catalyst loading. Indian Head and Velva lignites from North Dakota, Martin Lake lignite from Texas, Wyodak subbituminous coal from Wyoming and River King bituminous coal from Illinois were evaluated. Proximate and ultimate analyses of these coals are given in Table 1. The coal analyses in Table 1 show an uncharacteristically low moisture content for Indian Head lignite. The low moisture content of this sample, 12.6 wt%, resulted from storage in a large nitrogen purged bunker in which a definite moisture gradient was observed from top to bottom, but did not effect the reactivity of the char.

Table 1. Coal Proximate and Ultimate Analysis

	<u>Indian Head</u>		<u>Velva</u>	<u>Martin</u>	<u>Wyodak</u>	<u>River</u>
	<u>A^a</u>	<u>B^b</u>		<u>Lake</u>		<u>King</u>
<u>Test Coal Analyses:</u>						
Moisture, %	12.6	29.5	33.7	25.1	27.5	11.5
Ash, wt%, mf	17.7	9.0	10.4	22.1	9.6	12.1
Volatile Matter, wt%, mf	38.4	41.2	42.8	39.5	42.3	42.5
Fixed Carbon, wt%, mf	43.9	49.8	46.8	38.4	48.1	45.3
Heating Value, Btu/lb, as-rec'd	8,383	7,721	6,755	7,258	8,043	11,000
<u>Ultimate Analysis of</u>						
<u>Raw Coals, wt%, mf:</u>						
Ash	17.7	9.0	10.4	22.1	9.6	12.2
Carbon	58.9	65.0	62.4	56.7	65.7	68.3
Hydrogen	3.3	4.2	3.8	3.8	4.3	5.1
Nitrogen	1.6	1.9	1.4	1.2	1.2	1.3
Sulfur	1.0	0.8	0.5	1.9	0.5	4.0
Oxygen (by diff)	17.5	19.1	21.5	14.3	18.7	9.1

^aLow-moisture Indian Head coal used for majority of TGA work.

^bIndian Head sample used to verify initial TGA results.

Various alkali sources were tested as catalysts to promote the steam-carbon reaction. These were K_2CO_3 , Na_2CO_3 , trona, nahcolite, sunflower hull ash (a naturally high potassium containing ash), and recycled lignite gasification ash. These substances were selected as prospective catalysts based on their high alkali content. Catalysis with inexpensive or "disposable" catalysts would substantially improve the economics of a hydrogen-from-coal process. Likewise, trona and nahcolite, naturally occurring alkali carbonate materials, are inexpensive relative to pure carbonates (0.04/lb for trona compared to 0.34/lb for K_2CO_3 and 0.20/lb for Na_2CO_3). This cost differential suggests their use as disposable catalysts.

Reactivity of Coals for Steam Gasification

Tests were performed to establish the uncatalyzed reactivities of the five test coal chars and plotted in Figure 2. It shows the higher reactivity of low-rank coals compared to that of River King bituminous coal. The higher reactivity of low-rank coal chars, documented by many research groups (3,4,5), is believed to be a result of the higher mineral content, higher concentrations of active sites and increased porosity of the low-rank coals. Figure 2 also illustrates the linearity of conversion over the 0 to 50 % carbon conversion range.

Over the initial linear portion of the curves in Figure 2, the carbon conversion rates for the three lignites were nearly identical, with Indian Head being only slightly less reactive than the Velva and Martin Lake lignites. However, a definite hierarchy of reactivity developed as the available carbon supply was depleted. During reaction of the final 40% of the carbon, Martin Lake lignite showed the most rapid conversion, followed by Velva and Indian Head.

Steam gasification kinetic data was collected over the range of 700° to 800°C for assessing temperature effects. The increase in reactivity of each LRC with increasing temperature is shown in Figure 3. Increasing the gasification temperature from 700° to 800°C was found to increase reactivities from 2.5 times for Martin Lake lignite to 3.8 times for Wyodak subbituminous coal. Equilibrium gas composition modeling and actual product gases from a 1-lb fixed-bed system showed that the hydrogen content of the gas is virtually unaffected by this temperature increase (17). Apparent energies of activation were also calculated from this data and have been reported previously (18).

Steam Gasification of Catalyzed Coals

Figure 4 shows the rates of carbon conversion at 750°C for each test coal with a 10 wt% K_2CO_3 loading. Comparison of the data in Figure 2 to that in Figure 4 shows that K_2CO_3 addition significantly enhanced the reactivity of each coal. As was the case for the uncatalyzed coals, the reactivity of the catalyzed low-rank coals was far superior to that of the K_2CO_3 -catalyzed bituminous coal. However, the reactivity ranking of the four low-rank coals was not the same as that observed without catalyst addition. In Figure 2 Martin Lake lignite was shown to have the most rapid uncatalyzed conversion rate; however, in Figure 4, Martin Lake was shown to have the poorest reactivity of the four similarly catalyzed low-rank coals. Conversely, Wyodak subbituminous coal was the least reactive uncatalyzed low-rank coal, but showed excellent carbon conversion rates in tests using K_2CO_3 .

The effect of temperature on the reactivity of each of the four K_2CO_3 -catalyzed low-rank coals is illustrated in the bar graph of Figure 5. The trend in reactivity of the K_2CO_3 -catalyzed coals with a temperature increase from 700° to 800°C was very similar to that shown for the uncatalyzed coals in Figure 3, with reactivity increasing by a factor of two over the temperature range. For the uncatalyzed coals, the average reactivity increased by a factor of three over this temperature range. It has previously been reported that the addition of K_2CO_3 decreased the apparent energies of activation by as much as 60% compared to the uncatalyzed coals (18).

Several TGA steam gasification tests were performed to evaluate the effect of K_2CO_3 concentration on lignite reactivity. Velva lignite was used for these tests as it resulted in the highest reactivity of the four LRCs tested. Tests were conducted at 750°C using catalyst loadings from 2 to 20 wt%. Data collected from these experiments were used both to evaluate the effect of catalyst loading for each of the two carbonates, and to compare the two carbonates catalytic effect over a range of loadings. Table 2 presents the average reactivities at 50% carbon conversion for the range of loadings evaluated with both K_2CO_3 and Na_2CO_3 , which indicates a lesser dependence of reaction kinetics on catalyst loading using Na_2CO_3 . Neither catalyst produced a significant rate increase at loadings over 10 wt%; however, the reactivity increase with increasing catalyst loading upto 10 wt% was more pronounced for K_2CO_3 catalysis. Over the 2 to 10 wt% loading range, reactivity values for K_2CO_3 -catalyzed Velva lignite increased from 3.3 to 5.5 (g/hr)/g, while the corresponding increase for the Na_2CO_3 -catalyzed lignite was from 4.8 to 5.5 (g/hr)/g.

Table 2. Effect of Variable Catalyst Loadings on Velva Lignite Char Reactivity in Steam at 750°C

Catalyst Loading wt% of As-received Coal	$\bar{K}_{0.5}$, (g/hr)/g	
	K_2CO_3	Na_2CO_3
0	2.0	2.0
2	3.3	4.8
5	4.1	4.9
10	5.5	5.5
15	5.7	5.9
20	5.7	6.1

Comparison of Catalyst Effectiveness

Data plotted in Figure 6, compares carbon conversion rates for uncatalyzed Velva lignite and for Velva catalyzed with each of the six additives found to give positive catalytic effects. The nearly identical reactivities observed for K_2CO_3 and Na_2CO_3 catalysis are illustrated, as the two conversion curves are superimposable throughout the gasification phase. Figure 6 also illustrates the catalytic effects of sunflower hull ash and the mineral additives. Twenty percent sunflower hull ash (23 wt% potassium) was less effective than 10% loadings of the carbonates; however, reactivity was much improved over the uncatalyzed coal, with complete conversion occurring in less than 20 minutes. The reactivity for the 20% sunflower hull ash/Velva lignite system at 750°C was 4.3 (g/hr)/g as compared to only 2.0 (g/hr)/g without additives.

Perhaps the most significant results illustrated in Figure 6 were the rapid carbon conversions obtained using trona and nahcolite as gasification catalysts. Both trona and nahcolite produced more rapid conversion of Velva lignite than did addition of the pure carbonates. Approximately 90% carbon conversion was achieved in 8 minutes using either 10 wt% trona (29% sodium) or nahcolite (15% sodium), whereas when using the same wt% pure K_2CO_3 (47% potassium) or Na_2CO_3 (37% sodium) about 10 minutes was required to achieve 90% conversion. For trona catalysis a reactivity of 6.9 (g/hr)/g was obtained compared to 5.5 (g/hr)/g using an identical loading of either K_2CO_3 or Na_2CO_3 at the same gasification conditions. At these conditions, nahcolite catalysis resulted in a reactivity slightly lower than that obtained using trona (6.2 (g/hr)/g).

The effectiveness of these naturally occurring mineral catalysts is important to the development of a commercial hydrogen-producing steam coal gasification process. Based on the relative costs of the feedstock, use of these materials would be more favorable to process economics than would pure alkali carbonates. An additional consideration is that cost and availability of these materials may be such that catalyst recovery would be unnecessary.

Conclusions

Uncatalyzed lignites and a subbituminous coal were found to be eight to ten times more reactive with steam at 700°-800°C than an Illinois bituminous coal. This relationship, within this narrow temperature range, is important as this is the range that thermodynamically favors the production of hydrogen from steam gasification at atmospheric pressure. The reactivity of the uncatalyzed coals increased 3 to 4 times with an increase in steam gasification temperature from 700° to 800°C.

For the catalyzed coals during steam gasification:

- o Reactivity increased approximately 2 times over the 700° - 800°C temperature range for low-rank coals catalyzed with potassium carbonate.
- o Sodium carbonate was found to be as effective a catalyst as potassium carbonate for the steam gasification of low-rank coal chars on a mass loading basis.
- o Alkali carbonate loadings equal to 10 wt% of the as-received coal mass resulted in low-rank coal reactivities 2.5 to 3.5 times higher than those measured for the uncatalyzed low-rank coals.
- o Naturally occurring mineral sources of sodium carbonates/bicarbonates, trona and nahcolite, are as effective in catalyzing low-rank coal steam gasification as the pure carbonates.
- o Use of these naturally-occurring carbonates sources should be a primary focus of continued research. The low cost of trona or nahcolite relative to the pure carbonates suggests that a potential for their use as disposable catalysts exists which would enhance operability and process economics in a hydrogen-from-coal gasification process.

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References

1. Pohani, B.P. J. Japan Petrol. Inst., 27, 1, 1984.
2. Low-Rank Coal Research, University of North Dakota Energy Research Center, Quarterly Technical Progress Report, July-September, 1984, DOE/FE/60181-1682.
3. Johnson, J.L. "Kinetics of Coal Gasification." Wiley and Sons, New York, 1979, 324 pp.
4. Linares-Solano, O.P. Mahajan, and P.L. Walker. Fuel, 58, 327, 1979.
5. Walker, P.L., S. Matsumoto, T. Hanzawa, T. Muira, and I.M.K. Ismail. Fuel, 62, 140, 1983.
6. Euker, C.A. and R.D. Wesselhoft. Energy Progress, 1, 12, 1981.
7. Taylor, H.S. and H.J. Neville, J. Am. Chem. Soc., 43, 2055, 1921.
8. Dent, F.J. et al., Trans. Instn. Gas Engrs., 88, 150, 1938.
9. Weller, S. and Pelipetz, M.C., Ind. Energy Chem., 43, 243, 1951.
10. Walker, P.L. et al., Chem. and Phy. of Carbon, 4, 287, 1968.
11. Haynes, W.P. et al., ACS Div. Fuel Chem. Proc., 18, No.2, 1, 1973.
12. Willson, W.G. et al., Adv. in Chem.-Coal Gasif., 154, 203, 1974.
13. Veraa, M.J. and A.T. Bell, Fuel, 57, 194, 1978.
14. Serageldin, M.A. and W.P. Pan, Thermochimica Acta, 76, 145, 1984.
15. Radovic, L.R. et al., Fuel, 63, 1028, 1984.
16. Tomita, A. et al., Fuel, 62, 150, 1983.
17. Low-Rank Coal Research. University of North Dakota Energy Research Center, Quarterly Technical Progress Report, April-June 1984, DOE/FE/60181-1642.
18. Timpe, R.C. et al., ACS Div. Fuel Chem., 30, No.4, 481, 1985.

THERMOGRAVIMETRIC ANALYZER

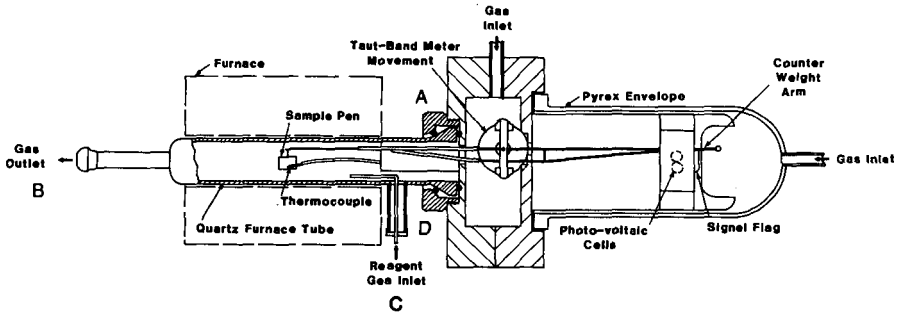


Figure 1. Thermogravimetric analyzer.

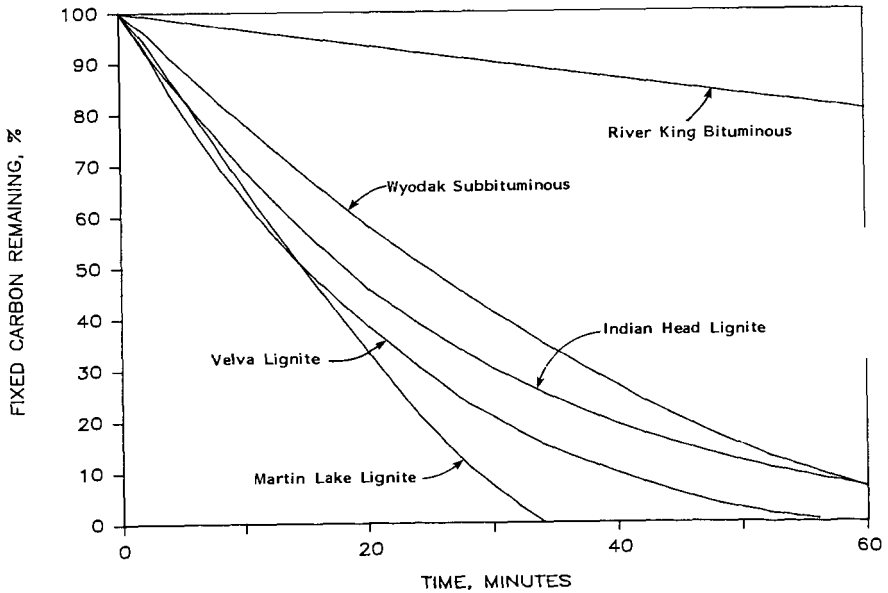


Figure 2. Rate of carbon conversion at 750°C - variation with coal rank.

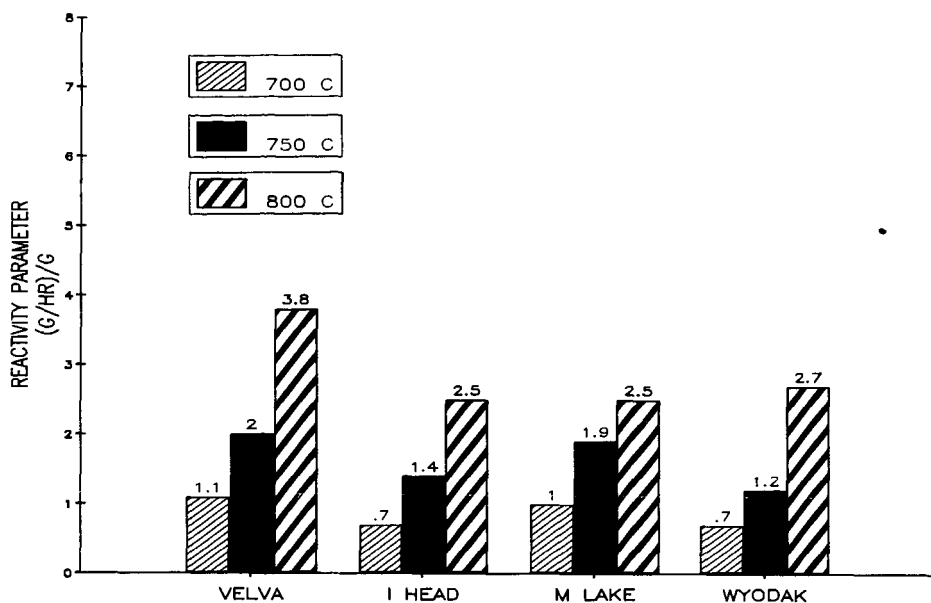


Figure 3. Reactivity of uncatalyzed low-rank coal chars as a function of steam gasification temperature.

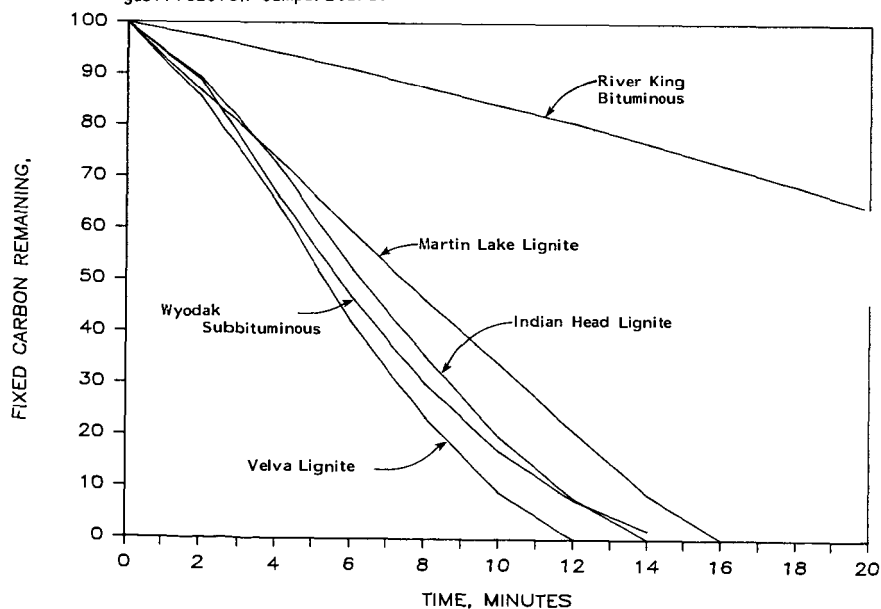


Figure 4. Carbon conversion of K_2CO_3 -catalyzed coal chars at 750°C.

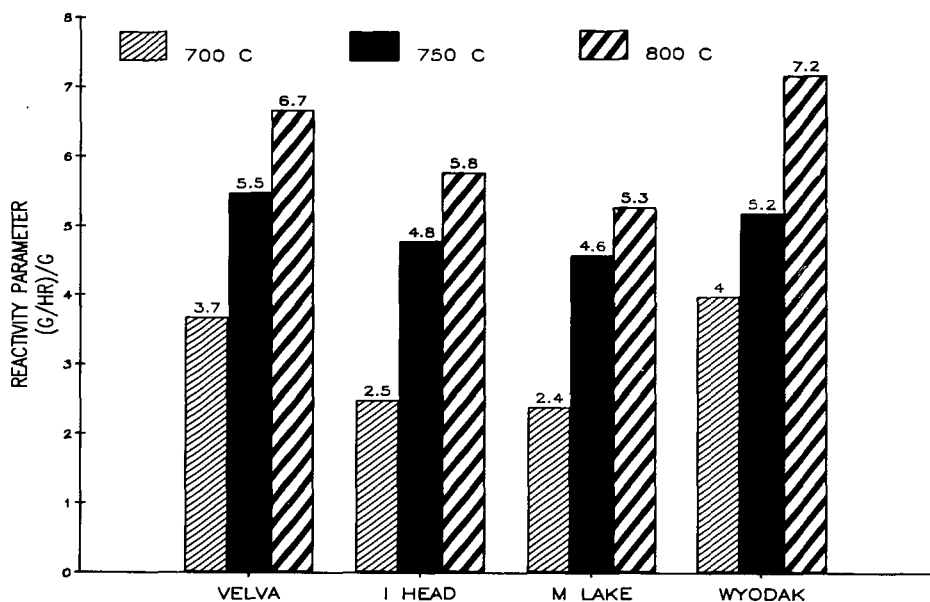


Figure 5. Effect of steam gasification temperature on the reactivity of K_2CO_3 -catalyzed low-rank coal chars.

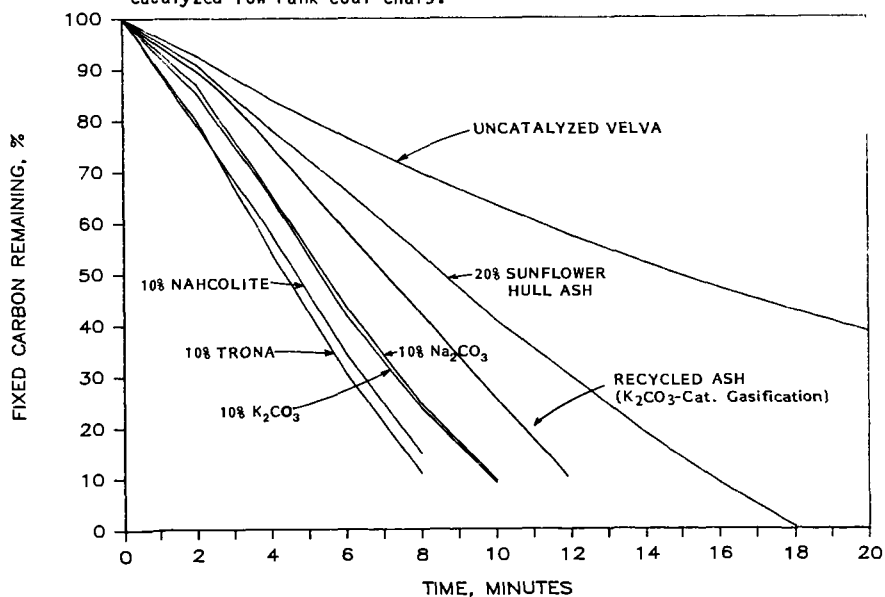


Figure 6. Rate of carbon conversion at 750°C for Velva lignite char catalyzed with various alkali sources.